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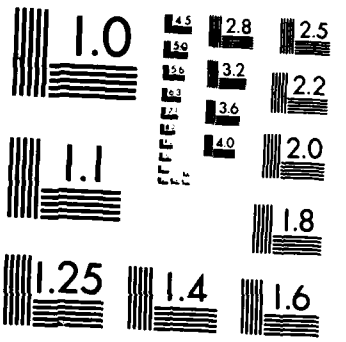

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Theoretical Study of Pulsed-Laser-Induced Resonant Desorption

by

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Theoretical Study of Pulsed-Laser-Induced Resonant Desorption

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Abstract

Adsorbed atoms irradiated by an infrared laser in resonance with one pair of vibrational levels of the adbond are studied. A pulsed laser is considered which has pulse duration short compared to the relaxation times of the system. The equations governing the time evolution of the adbond under a series of π-pulses are derived. Two criteria are defined to compare the effects of a series of π-pulses and of a continuous-wave laser. They are: (1) equal average energy in both lasers and (2) equal average resonant heating due to both lasers. These criteria are used to compare the effects of a pulsed laser and a continuous-wave laser on laser-induced resonant desorption. It is shown that a pulsed laser does not lead to a dramatic increase of the desorption. In the high-intensity limit, resonance heating and desorption reach the same saturation limit for a pulsed laser as for a continuous-wave laser.

1. Introduction

When a coated surface is irradiated by a laser, the laser frequency can be chosen such that it is in resonance with one of the transitions of the adbond. If the substrate is transparent at that frequency, the primary effect of the laser is to bring the adsorbed particle into an excited state. In this way, the laser may influence desorption and other surface processes.

Due to the interaction of the adparticle with the substrate degrees of freedom, relaxation of the excited state will occur. This will limit the probability of finding the adparticle in an excited state of the adbond. Also, it means that there is an energy flow from the laser into the substrate, a process called resonant heating.[1] In a previous paper it was shown that this is in fact the most important process occurring, i.e., almost all of the absorbed laser energy is used for heating the substrate rather than for desorption.[2] If the heat conductivity of the substrate is not large enough to divert the absorbed energy immediately, resonant absorption will lead to elevated surface temperatures, and consequently will lead to enhanced desorption.[3] In this way the laser indirectly influences the desorption process.

The resonant effect of laser absorption has been clearly established experimentally.[3-8] However, it is yet an unresolved question whether laser-induced resonant desorption or laser-induced thermal desorption via resonant heating can explain these experiments,[3,8] although there are strong indications that the experiments can be accounted for, at least partially, by resonant desorption. In this paper, we shall calculate both desorption and resonant heating. However, we will consider only direct resonant desorption, i.e., we assume that the thermal conductivity of the substrate is large enough to maintain a constant surface temperature.

Much theoretical effort has gone into studies of the effects of continuous-wave lasers on adspecies.[2,9-15] Experimentally, either continuous-wave lasers have been used or pulsed lasers with a pulse duration long compared to the relaxation times.[3,4,7,8,16,17] This means that for the laser-adbond dynamics, the theory for continuous-wave lasers will also apply for these pulsed lasers.

In this paper, we shall consider the effect of a short laser pulse on the dynamics of an adatom. A short pulse is defined as a pulse with a duration much shorter than the energy relaxation time (T_1) of the excited levels. Then, during the action of the pulse, the relaxation can be neglected, and the effect of the pulse is to change the occupation probabilities and coherences of the two coupled levels.[18] Relaxation, desorption and other possible surface processes occur after the pulse as free evolution of the adspecies system under the initial conditions determined by the effect of the pulse. We shall derive the equations of motion describing the time evolution of the reduced density matrix of the adbond for a series of equally spaced π-pulses.

Of particular interest is the comparison of the effect of a series of short pulses with the effect of a continuous-wave laser. We shall do so by calculating the average desorption for both cases. The key point here is the criterion used for comparing both lasers. We shall use two criteria. The first is to require that both lasers have the same average energy. The second is that both lasers must lead to the same average energy flux into the substrate. It will follow that these two criteria lead to completely different requirements for the available power in both lasers.

2. Pulsed Laser Adbond Dynamics

Consider an adsorbed atom or molecule irradiated by a laser beam with frequency ω_L. Assume that the laser is in resonance with but one pair of vibrational levels of the adbond. Then, for pulses short compared to the energy relaxation times of the system, the time evolution is given by the optical Bloch equations:[18]

$$\begin{aligned} \frac{dR_1}{dt} &= \Delta R_2 \\ \frac{dR_2}{dt} &= -\Delta R_1 + \Omega_p(t) R_3 \\ \frac{dR_3}{dt} &= -\Omega_p(t) R_2 . \end{aligned} \tag{2.1}$$

Here $\Omega_p(t) = \frac{1}{\hbar}\vec{\mu}\cdot\vec{E}_o(t)$ is the time-dependent Rabi frequency; $\vec{E}(t) = \vec{E}_o(t)\cos(\omega_L t)$ is the classical electric field amplitude of the laser, with slowly-varying envelope $\vec{E}_o(t)$; $\vec{\mu}$ is the transition dipole of the adbond; $\Delta = \omega_L - (\omega_e - \omega_g)$ is the detuning; and $\hbar\omega_g$ and $\hbar\omega_e$ are the energy of the ground level and the excited level, respectively. The real-valued quantities R_1, R_2 and R_3 are defined by the populations of and coherences between the two coupled levels in the rotating frame, according to

$$\begin{aligned} R_1 &= \bar{P}_{ge} + \bar{P}_{eg} \\ R_2 &= -i(\bar{P}_{ge} - \bar{P}_{eg}) \\ R_3 &= P_e - P_g . \end{aligned} \tag{2.2}$$

For nonzero detuning, analytical solutions to Eq.(2.1) exist only for a few special pulse shapes $E_o(t)$.[18,19] For zero detuning the solution is easily obtained. It does not depend on the pulse shape, but only on the integral,

$$\Theta(t) = \int_{-\infty}^{t} dt' \Omega_p(t'). \tag{2.3}$$

Since we are only interested in the populations after the pulse, the integral in Eq.(2.3) can be extended over the complete pulse to obtain the pulse area Θ, which is then independent of time. In this paper only zero detuning will be considered. The values of R_1, R_2 and R_3 directly after the pulse are,[18]

$$\begin{aligned} R_1(\Delta t) &= R_1^o \\ R_2(\Delta t) &= R_2^o \cos(\Theta) + R_3^o \sin(\Theta) \\ R_3(\Delta t) &= R_3^o \cos(\Theta) - R_2^o \sin(\Theta). \end{aligned} \tag{2.4}$$

The start of the pulse is taken as the zero point of time. The pulse duration is given by Δt, and R_1^o, R_2^o and R_3^o are the values of R_1, R_2 and R_3 directly before the pulse. From Eq.(2.4) it follows that maximum inversion R_3 is obtained for pulses with a value of Θ equal to π. Since we are interested in an optimal effect, that is, the maximal value for P_e, we shall consider only π-pulses in this paper.

Assume that the system is initially in thermal equilibrium, i.e., $R_1 = 0$, $R_2 = 0$ and $R_3 = R_3(eq)$. Then, after a π-pulse, $R_1 = R_1(\Delta t)$ and $R_2 = R_2(\Delta t)$ are zero again, whereas R_3 is changed to

$$R_3(\Delta t) = -R_3(eq). \tag{2.5}$$

Between two consecutive pulses the adbond evolves freely through its relaxation against the substrate degrees of freedom. The off-diagonal elements of the reduced density matrix of the adbond decay exponentially to zero,[15] and because they were initially zero, they remain zero throughout. The time evolution of the diagonal elements is described by the master

equation

$$\frac{dP_n(t)}{dt} = \sum_k \{W_{kn}P_k(t) - W_{nk}P_n(t)\}, \tag{2.6}$$

where the summation extends over all vibrational levels of the adbond, including those not involved in the coupling to the laser. W_{nk} is the rate constant for the transition from state n to state k, which can be obtained, for example, through second-order perturbation theory.[15,20,21] The populations, $P_n(t)$, can be obtained by solving Eq. (2.5) under the initial conditions given by the result of the pulse, $P_n(\Delta t)$.

Consider the case where the adspecies is irradiated by a series of equally-spaced π-pulses, with interval time t_p. Then, after several pulses, a quasi steady state will be reached, wherein the time evolution in each interval t_p will be the same. The formal solution of Eq. (2.6) is $(\Delta t \leq t \leq t_p)$,

$$\underset{\sim}{P}(t) = \underset{\sim}{P}(eq) + e^{-\underset{\approx}{W}(t-\Delta t)}[\underset{\sim}{P}(\Delta t) - \underset{\sim}{P}(eq))], \tag{2.7}$$

where $\underset{\approx}{W}$ is the matrix formed by the transition rates W_{nk}, and has elements

$$\underset{\approx}{W}_{nm} = +\sum_k W_{nk}\delta_{nm} - W_{mn}. \tag{2.8}$$

$\underset{\sim}{P}(t)$ is the vector formed by the occupation probabilities $P_n(t)$, and $\underset{\sim}{P}(eq)$ is the equilibrium solution of Eq. (2.6). Of course $\underset{\sim}{P}(eq)$ can be omitted from Eq. (2.7). However, to clearly demonstrate the thermal and the laser effect, we have written it as it is. In the quasi steady state, Eq. (2.7) gives a relation between the $P_n(\Delta t)$ and $P_n(t_p)$ of

$$\underset{\sim}{P}(t_p) = \underset{\sim}{P}(eq) + e^{-\underset{\approx}{W}t_p}[\underset{\sim}{P}(\Delta t) - \underset{\sim}{P}(eq)], \tag{2.9}$$

where we have used that $\exp[-\underset{\approx}{W}\Delta t] = 1$. Alternatively, the effect of the pulse is known from Eq. (2.5), which gives

$$\begin{aligned} P_n(t_p) &= P_n(\Delta t) = P_n^o \qquad (n \neq e,g) \\ P_g(t_p) &= P_e(\Delta t) = P_g^o \\ P_e(t_p) &= P_g(\Delta t) = P_e^o. \end{aligned} \tag{2.10}$$

Equations (2.9) and (2.10) together define the quantities $P_n(t_p)$ and $P_n(\Delta t)$ in terms of the system parameters W_{nk} and the time t_p. They therefore provide the initial condition to be used in Eq. (2.7). A schematic drawing of the time evolution in the quasi steady state is given in Fig. 1.

3. Continuous-Wave Laser

Again, we consider a laser in resonance with only two vibrational levels of the adbond. For a continuous-wave laser, the equation of motion for the reduced density matrix of the adbond is[20]

$$\begin{aligned} \frac{dP_n(t)}{dt} &= \sum_k \{W_{kn}P_k(t) - W_{nk}P_n(t)\} \quad (n \neq e,g) \\ \frac{dP_g(t)}{dt} &= \sum_k \{W_{kg}P_k(t) - W_{gk}P_g(t)\} + \tfrac{1}{2}\Omega_{CW}R_2(t) \\ \frac{dP_e(t)}{dt} &= \sum_k \{W_{ke}P_k(t) - W_{ek}P_e(t)\} - \tfrac{1}{2}\Omega_{CW}R_2(t) \\ \frac{dR_2(t)}{dt} &= -\sum_k \tfrac{1}{2}(W_{ek} + W_{gk})R_2(t) + \Omega_{CW}(P_e(t) - P_g(t)) - \Delta R_1(t) \\ \frac{dR_1(t)}{dt} &= -\sum_k \tfrac{1}{2}(W_{ek} + W_{gk})R_1(t) + \Delta R_2(t), \end{aligned} \tag{3.1}$$

where the symbols have the same meaning as in Eqs. (2.1), (2.2) and (2.6), and Ω_{CW} is the time independent Rabi frequency of the continuous wave laser. For the rate constants W_{nk}, the expressions derived by Efrima et al.[21] or Arnoldus et al.[15] can be used. Equations similar to Eq. (3.1) can be

obtained for the other coherences. They are not coupled to Eq. (3.1) and therefore need not be considered here.

We are interested in the long-time behavior of the system, i.e., only the steady-state solution of Eq. (3.1) is needed. Then the occupation probabilities follow from

$$\sum_k W_{nk} P_n(\infty) = \sum_k W_{kn} P_k(\infty) \quad (n \neq e,g)$$

$$\sum_k W_{gk} P_g(\infty) = \sum_k W_{kg} P_k(\infty) - \tfrac{1}{2} \frac{\Gamma_{eg}}{\tfrac{1}{2}\Gamma_{eg}^2 + 2\Delta^2} \Omega_{CW}^2 [P_g(\infty) - P_e(\infty)] \tag{3.2}$$

$$\sum_k W_{ek} P_e(\infty) = \sum_k W_{ke} P_k(\infty) + \tfrac{1}{2} \frac{\Gamma_{eg}}{\tfrac{1}{2}\Gamma_{eg}^2 + 2\Delta^2} \Omega_{CW}^2 [P_g(\infty) - P_e(\infty)]$$

with $\Gamma_{eg} = \sum_k (W_{ek} + W_{gk})$ and $P_n(\infty)$ denotes the steady-state value of $P_n(t)$.

4. Pulsed Laser and Continuous-Wave Laser

To be able to compare the effects of a pulsed laser and the effects of a continuous-wave laser, a criterion is necessary for comparing these two lasers. One possibility is to require that the total average energy in the continuous-wave laser and in the series of pulses be equal. Because the intensity of a laser is proportional to the square of the electric field amplitude, and the Rabi-frequency is proportional to the amplitude of the electric field itself, this leads to the condition:

$$\frac{1}{t_p} \int_0^{\Delta t} dt\, \Omega_p^2(t) = \Omega_{CW}^2 , \tag{4.1}$$

where it is assumed that the constants of proportionality are the same in both cases. For a π-pulse we have also the condition,

$$\theta = \int_0^{\Delta t} dt\ \Omega_p(t) = \pi. \tag{4.2}$$

For a given average laser intensity, Ω_{CW}^2, Eqs. (4.1) and (4.2) together give a relation between the pulse duration Δt and the pulse interval time t_p. For a square pulse, that relation is

$$\Delta t \cdot t_p = \frac{\pi^2}{\Omega_{CW}^2}. \tag{4.3}$$

Further restrictions are $\Delta t \ll t_p$ and $\Delta t \ll \Gamma^{-1}$, with Γ^{-1} a typical relaxation time. Therefore, Eqs. (4.1)-(4.3) severely limit the number of available pulses for a given intensity.

A second criterion for comparing the effects of the two lasers is to require that the average energy flow into the substrate (resonant heating) is equal in both cases, which is almost equivalent to requiring that the total absorption from the lasers be equal.[2] For the continuous-wave laser the energy flow in the steady state is constant in time. Per unit of time it is given by,[2]

$$\frac{dE_{CW}}{dt} = \hbar\omega_L \frac{\frac{1}{2}\Gamma_{eg}}{\frac{1}{2}\Gamma_{eg}^2 + 2\Delta^2} \Omega_{CW}^2 \left(P_g(\infty) - P_e(\infty)\right). \tag{4.4}$$

For the pulsed laser the average absorption in the quasi steady state can simply be obtained from Eq. (2.10) as

$$\frac{\Delta E_p}{t_p} = \hbar\omega_L \frac{1}{t_p}(P_g^o - P_e^o). \tag{4.5}$$

Combination of these two equations gives

$$\frac{1}{t_p}(P_g^o - P_e^o) = \frac{\Omega_{CW}^2}{\Gamma_{eg}} \left[P_g(\infty) - P_e(\infty)\right], \tag{4.6}$$

where we have set $\Delta = 0$. The populations P_g^o and P_e^o can be expressed in terms of the rate constants and the interval time t_p by use of Eqs (2.9) and (2.10). The steady-state solutions $P_g(\infty)$ and $P_e(\infty)$ follow from Eq. (3.2) and are a function of the transition probabilities and the Rabi frequency Ω_{CW}.

5. Desorption

Desorption can be described by the addition of a loss term, $-W_{nc}P_n(t)$, to each of the master equations, Eqs. (2.6) and (3.1). Previously, the loss rates were defined as the rate constant for the transition from the bound state n to any of the continuum states of the adbond potential.[21] However, the results presented here are not restricted to such an interpretation.

Here we consider only slow desorption, which allows the use of the populations for the steady-state and the quasi steady-state as determined by Eqs. (3.1) and (2.6), respectively. With these occupation probabilities the average rate of desorption is defined as,

$$D = \frac{1}{(t_p - \Delta t)} \int_{\Delta t}^{t_p} dt \sum_n W_{nc} P_n(t), \tag{5.1}$$

where by the nature of the assumptions made earlier the integral can be taken either from Δt to t_p or from 0 to t_p. To obtain the average desorption for the pulsed laser and for the continuous-wave laser, the respective functions $P_n(t)$ have to be substituted in Eq. (5.1).

The ratio between the pulsed-laser desorption and the continuous-wave-laser desorption is a measure of the effectiveness of the one over the other. This ration, μ, can be written as

$$\mu = \frac{\sum_n W_{nc} P_n(av)}{\sum_n W_{nc} P_n(\infty)}, \tag{5.2}$$

where $P_n(av)$ is the average occupation probability for the pulsed irradiated adbond given as

$$P_n(av) = \frac{1}{(t_p - \Delta t)} \int_{\Delta t}^{t} dt\, P_n(t), \tag{5.3}$$

and $P_n(\infty)$ is the steady state occupation probability for the continuous wave laser case.

For a continuous-wave laser, the high-intensity limit is defined by $\frac{\Omega_{CW}^2}{\Gamma_{eg}^2} \to \infty$, for the pulsed laser the high-intensity limit corresponds to $\Gamma t_p \to 0$. Note that for the idea of a pulsed laser to be valid, the latter limit has to be taken under the condition $\Delta t \ll t_p$. It is easily shown that the occupation probabilities, the energy flux and desorption assume saturation values in the high-intensity limit. In the high-intensity limit the occupation probabilities for the pulsed laser and for the continuous-wave laser obey the same set of equations

$$\sum_k W_{nk} P_n = \sum_k W_{kn} P_k \tag{5.4}$$

$$P_g = P_e.$$

For a pulsed laser, Eq. (5.4) refers to $P_n(av) = P_n(\Delta t)$, and they are valid apart from a term of the order of Γt_p. For a continuous-wave laser, Eq. (5.4) refers to $P_n(\infty)$, and they are valid apart from terms of the order of $\left(\frac{\Omega_{CW}^2}{\Gamma_{eg}^2}\right)^{-1}$. It follows immediately that the desorption for both situations

is the same, i.e., $\mu = 1$ [Eq. (5.2)]. The saturation limit for the energy flux is also the same, and can be written as

$$\frac{dE_{CW}}{dt} = \frac{\Delta E_p}{t_p} = \hbar\omega_L \sum_k \{W_{kg}P_k - W_{gk}P_g\}. \tag{5.5}$$

This means that use of criterion 2 leads to $\mu = 1$ in the high-intensity limit. Criterion 1 (equal average laser intensity) is defined by [Eq. (4.3)]

$$\frac{\Gamma_{eg}\Delta t}{\pi^2}\Gamma_{eg}t_p = \left(\frac{\Omega_{CW}^2}{\Gamma_{eg}^2}\right)^{-1}, \tag{5.6}$$

One of our basic assumptions is $\frac{\Gamma_{eg}\Delta t}{\pi^2} \ll 1$. Therefore, if we take $\frac{\Omega_{CW}^2}{\Gamma_{eg}^2} \equiv \left(\frac{\Gamma_{eg}\Delta t}{\pi^2}\right)^{-1} \gg 1$, $\Gamma_{eg}t_p$ is about one. It follows that the saturation limit is reached for the continuous-wave laser at a much lower average intensity than for the pulsed laser. It can be concluded that in the high-intensity limit the pulsed laser is not more effective than the continuous-wave laser, whereas from an energetic point of view the continuous-wave laser will always be the best choice.

A weak continuous-wave laser is defined by $\frac{\Omega_{CW}^2}{\Gamma_{eg}^2} \ll 1$. In that limit the populations are different from their equilibrium values by a term proportional to the laser intensity, i.e.,

$$P_n(\infty) = P_n(eq) + C_n \frac{\Omega_{CW}^2}{\Gamma_{eg}^2}, \tag{5.7}$$

where C_n are constants. For $(\frac{\Omega_{CW}^2}{\Gamma_{eg}^2})<<1$, we also have [Eqs. (4.3) and (4.6)]$\Gamma_{eg}t_p>>1$. Then, the pulsed-laser-induced desorption can approximately be evaluated from

$$P_n(av) = P_n(eq) + \frac{1}{\Gamma t_p}\{P_n(\Delta t) - P_n(eq)\}, \tag{5.8}$$

where Γ is in the range of the nonzero eigenvalues of $\underline{W}$. The situation we are interested in the situation where the laser gives a considerable enhancement of the desorption. This means that the pure thermal desorption can be neglected. An approximate expression for μ is then

$$\mu = \frac{\sum_n W_{nc}[P_n(\Delta t) - P_n(eq)]}{\sum_n W_{nc}C_n} \; \frac{\frac{1}{\Gamma_{eg}t_p}}{\frac{\Omega_{CW}^2}{\Gamma_{CW}^2}} \tag{5.9}$$

Since we do not know the constants C_n, an estimate for μ cannot be made. However, it does follow from Eq. (5.9) that both criteria for comparing the lasers [Eqs. (4.3) and (4.6)], lead to a μ which is independent of the laser power. For criterion 2 [Eq. (4.6)], μ becomes simply,

$$\mu = \frac{\sum_n W_{nc}[p_n(\Delta t) - P_n(eq)]}{\sum_n W_{nc}C_n}, \tag{5.10}$$

that is, μ is completely determined by system properties. For criterion 1 [Eq. (4.3)], a value less by a factor $\frac{\Gamma_{eg}\Delta t}{\pi^2}<<1$ is obtained. It is interesting to note that now μ becomes larger if the pulse duration becomes longer. Of course, the pulse duration is limited to values $(\Gamma_{eg}\Delta t) << 1$.

6. Two-Level System

A two-level system is of special interest because all the equations can be solved analytically, and values for the different quantities are obtained which depend only one relaxation time $\Gamma^{-1} = (W_{ge} + W_{eg})^{-1}$. There are only two states, the ground state $|g\rangle$ and the excited state $|e\rangle$, with the obvious relation between the populations of

$$P_e(t) + P_g(t) = 1. \tag{6.1}$$

For the pulsed-laser-irradiated adbond, it follows from Eqs. (2.7), (2.9) and (2.10) that

$$P_e(t) = P_e(eq) + \frac{[1 - 2P_e(eq)]}{[1 + e^{-\Gamma t_p}]} e^{-\Gamma t}, \tag{6.2}$$

with the equilibrium population given by

$$P_e(eq) = \frac{W_{ge}}{\Gamma}. \tag{6.3}$$

The average population of the upper level is [Eq. (5.3)]

$$P_e(av) = P_e(eq) + [1 - 2P_e(eq)] \frac{1}{\Gamma t_p} \frac{[1 - e^{-\Gamma t_p}]}{[1 + e^{-\Gamma t_p}]}. \tag{6.4}$$

The average energy flow into the substrate is obtained as [Eq. (4.5)]

$$\frac{\Delta E_p}{t_p} = \hbar\omega_L \Gamma \, P_e(av) \tag{6.5}$$

For the continuous-wave laser irradiation, the excited level population is,

$$P_e(\infty) = P_e(eq) + [1 - 2P_e(eq)] \, \tfrac{1}{2} \frac{\Omega^2_{cw}}{\tfrac{1}{2}\Gamma^2 + \Omega^2_{cw}}, \tag{6.6}$$

which is constant in time. The energy flow into the substrate is given by,

$$\frac{dE_{cw}}{dt} = \hbar\omega_L \frac{\Omega^2}{\Gamma} [1 - 2P_e(\infty)]. \tag{6.7}$$

The situation is considered where pure thermal desorption can be neglected, i.e., the adspecies is stable without the laser. Then, for desorption the first term in Eq. (6.2) and in Eq. (6.6) can be neglected, and the ratio between pulsed-laser-induced desorption and continuous-wave-laser-induced desorption becomes [Eq. (5.2)]

$$\mu = \frac{2}{[1 + e^{-\Gamma t_p}]} \frac{[1 - e^{-\Gamma t_p}]}{\Gamma t_p} \frac{[\frac{1}{2}\Gamma^2 + \Omega_{CW}^2]}{\Omega_{CW}^2} \tag{6.8}$$

This implies that in the strong laser limit ($\Gamma t_p \to 0$; $\frac{\Omega_{CW}^2}{\Gamma^2} \to \infty$) $\mu = 1$, as it should be. Also, for $\frac{\Omega_{CW}^2}{\Gamma^2} >> 1$ but $\Gamma t_p \neq 0$, it is easily shown that $\mu < 1$, with μ decreasing for increasing Γt_p. Using criterion 1, the ratio can be written as,

$$\mu = \frac{[1 - e^{-\Gamma t_p}]}{[1 + e^{-\Gamma t_p}]} \frac{\Gamma^2 + 2\Omega_{CW}^2}{\Gamma^2} \frac{\Gamma \Delta t}{\pi^2}, \tag{6.9}$$

which in the low-intensity limit leads to $\mu \approx \frac{\Gamma \Delta t}{\pi^2} << 1$. For Ω_{CW}^2/Γ^2 and/or Γt_p of the order unity, μ starts increasing, until it reaches its saturation value 1 in the high-intensity limit.

With the second criterion we obtain from Eqs. (6.5), (6.7) and (6.8) that μ equals unity, independent of the laser power used. Note that in this case μ is equal to the ratio of the quantum yield of desorption. Where the latter is defined as the number of photons used for desorption divided by the number of photons used for substrate heating.[2]

7. Conclusions

In this paper we have studied the dynamics of an adspecies irradiated by a series of equally-spaced π-laser pulses, in resonance with one pair of

vibrational levels of the adbond. The equations describing the time evolution of the reduced density matrix of the adbond are derived. A quasi steady state is defined as the state wherein the time evolution in each pulse interval is the same.

In particular, we have studied the laser-induced desorption and the resonant heating of the substrate. A comparison is made between the effects of a pulse train and of a continuous-wave laser. The essential point for making this comparison is how to relate both lasers. Two criteria are given which may serve for such a goal. The first is to require that both lasers have equal average energy. It is then found that the ratio between the pulsed-laser-induced desorption and the continuous-wave-laser-induced desorption [Eq. (5.2)] becomes proportional to $\Gamma\Delta t$ (low intensity limit), where Δt is the pulse duration. In other words, μ can be made arbitrarily small by decreasing the pulse duration. This result can be understood easily if one realizes that for one pulse the energy content is proportional to the intensity multiplied by the duration, whereas the total exciting power is only proportional to the product of Δt with the square root of the intensity [Eqs. (2.3) and (2.4)]. This should be compared with the continuous-wave laser case, where both the energy and the exciting power are proportional to the intensity [Eq. (3.2)]. This observation leads to an interesting prediction for the intensity dependence of the laser induced desorption. Experimentally, it has been found that the laser-induced desorption is proportional to some power, n, of the laser intensity, where n is interpreted as the number of photons necessary for providing the required desorption energy.[7] From the analysis here, it follows that for short pulses an exponent of $\frac{1}{2}n$ will be found.

The situation is considered where pure thermal desorption can be neglected, i.e., the adspecies is stable without the laser. Then, for desorption the first term in Eq. (6.2) and in Eq. (6.6) can be neglected, and the ratio between pulsed-laser-induced desorption and continuous-wave-laser-induced desorption becomes [Eq. (5.2)]

$$\mu = \frac{2}{[1 + e^{-\Gamma t_p}]} \frac{[1 - e^{-\Gamma t_p}]}{\Gamma t_p} \frac{[\frac{1}{2}\Gamma^2 + \Omega_{CW}^2]}{\Omega_{CW}^2} \tag{6.8}$$

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7. Conclusions

In this paper we have studied the dynamics of an adspecies irradiated by a series of equally-spaced π-laser pulses, in resonance with one pair of

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In particular, we have studied the laser-induced desorption and the resonant heating of the substrate. A comparison is made between the effects of a pulse train and of a continuous-wave laser. The essential point for making this comparison is how to relate both lasers. Two criteria are given which may serve for such a goal. The first is to require that both lasers have equal average energy. It is then found that the ratio between the pulsed-laser-induced desorption and the continuous-wave-laser-induced desorption [Eq. (5.2)] becomes proportional to $\Gamma\Delta t$ (low intensity limit), where Δt is the pulse duration. In other words, μ can be made arbitrarily small by decreasing the pulse duration. This result can be understood easily if one realizes that for one pulse the energy content is proportional to the intensity multiplied by the duration, whereas the total exciting power is only proportional to the product of Δt with the square root of the intensity [Eqs. (2.3) and (2.4)]. This should be compared with the continuous-wave laser case, where both the energy and the exciting power are proportional to the intensity [Eq. (3.2)]. This observation leads to an interesting prediction for the intensity dependence of the laser induced desorption. Experimentally, it has been found that the laser-induced desorption is proportional to some power, n, of the laser intensity, where n is interpreted as the number of photons necessary for providing the required desorption energy.[7] From the analysis here, it follows that for short pulses an exponent of $\frac{1}{2}n$ will be found.

The second criterion used is to require that the energy flux from the laser into the substrate is the same in both cases. Then it is found that in the low-intensity limit μ becomes independent of the laser power. Of course, to achieve this, a pulsed laser is required which is much more intense than the continuous-wave laser.

In the high-intensity limit, all quantities assume saturation values. It is shown that $\mu = 1$ in this case. From criterion 1 it follows that the high-intensity limit is reached for much lower average power by the continuous-wave laser than by the pulsed laser.

For a two-level system the equations can be solved analytically. It is found that criterion 2 leads to $\mu = 1$ for all laser powers. In the low-intensity limit criterion 1 gives $\mu \ll 1$. For increasing intensity, μ grows gradually to one.

In this paper it has been shown that use of a pulsed laser instead of a continuous-wave laser does not lead to a dramatic increase of resonant desorption or resonant heating. Basically this can be understood from the fact that both processes depend in some way on the average populations of the excited vibrational levels. These cannot be enhanced by using a pulsed laser. Other processes, like laser-induced thermal desorption via resonant heating, depend on the average of some function (e.g., exponential) of the occupation probabilities. It can be expected that then quite different results will be obtained.

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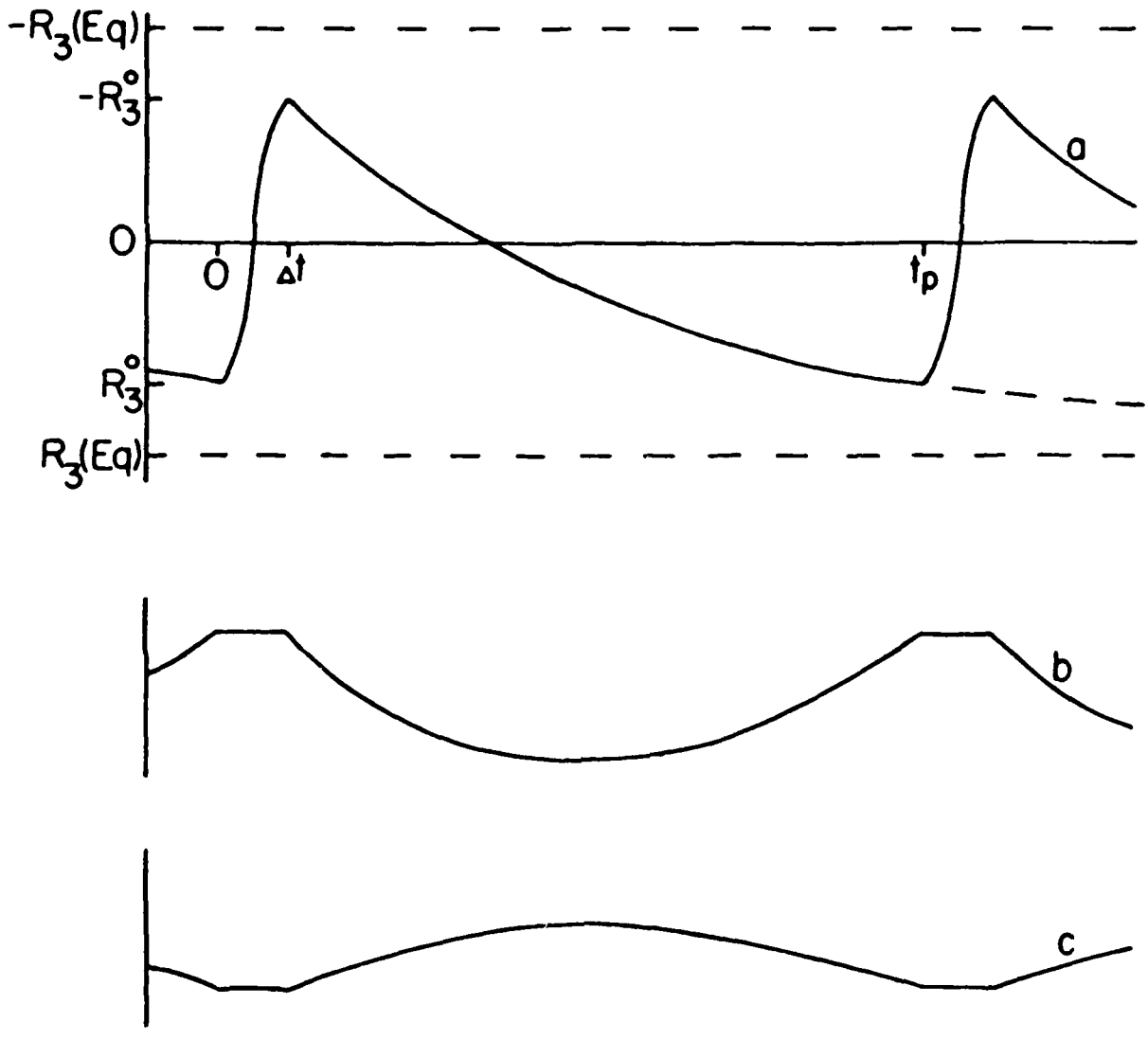
FIGURE CAPTION

Fig. 1: Schematic drawing of the time evolution of the vibrational level populations for a pulse sequence in the quasi steady state. Curve (a) represents the inversion $R_3 = P_e - P_g$; curve (b) represents $P_e + P_g$; and curve (c) represents the population of any other level $n \neq e$ or g. The actual variation of the populations during the pulse ($0<t<\Delta t$) depends on the pulse shape. For a two-level system there are no levels $n \neq e$ or g, and $P_e + P_g = 1$.

Figure 1.



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